FINAL REPORT

For the period June 12, 1966 through June 11, 1970

UNCLASSIFIED

1.	PROJECT TITLE	"Quantum Mechanical Calculations of Light Metal Diatomic Hydrides, Oxides and Halides"
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4.	CONTRACTOR	The University of Chicago Chicago, Illinois Tel: (312) NO7-4700
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9.	PROJECT SCIENTIST	Dr. Robert Mace (Durham) Tel: (919) 286-2285
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1.   Evaluation of Analytic Electronic Wavefunctions and Properties for
      Atoms and Molecules: Theoretical Development

The theoretical formulation, as well as computer programs for the
evaluation of Hartree-Fock wavefunctions and various properties of atomic and
molecular systems, has been completed. Extensive calculations, carried to the limit
of the Hartree-Fock independent particle model demonstrated the need for the explicit
inclusion of electron-electron correlation into the electronic wavefunction, if various
atomic and molecular properties were to be computed reliably. To this end the multi-
configuration self-consistent-field (MC-SCF) model was developed. In this model the
electronic wavefunction is represented by a linear combination of several Slater
determinants, rather than only one, as in the Hartree-Fock model, and all the orbitals,
as well as the configuration expansion coefficients, are determined simultaneously
using the variational principle. The development of this model proceeded in two
stages: first the method was restricted to pair replacement, i.e. the shell occupation
numbers in the different Slater determinants of the wavefunction had to differ by even
numbers. Later this restriction was removed and a completely general theory was
developed. Considerable effort was expended towards the development of stable
numerical procedures for the solution of the strongly coupled MC-SCF equations.
This development was completed successfully. Computer programs for the calculation
of MC-SCF wavefunctions for atoms and linear molecules were constructed and tested
extensively. The theory for the calculation of excited states of same symmetry as
lower lying states was developed. This has been incorporated into the MC-SCF

computer programs, thus the calculation of excited states, even if there are lower states of same symmetry, can be performed with equal ease and accuracy as the calculation of ground states.

Methods for the optimization of the nonlinear parameters, the orbital exponents, in analytical wavefunctions have been improved, thus allowing a more rapid accurate calculation of atomic and molecular wavefunctions. Also the calculation of wavefunctions for linear molecules has been made significantly more efficient through a completely new analysis of the required molecular integrals. This analysis was carried out in collaboration with Drs. McLean and Yosimine of IBM Research, and has lead to a molecular integrals program, which is significantly faster and more accurate than similar programs available heretofore.

2.   Calculation of Electronic Wavefunctions and Properties
        of Atoms and Molecules

Using the available Hartree-Fock computer programs, the calculation of analytical wavefunctions close to the Hartree-Fock limit has been completed for first and second row diatomic hydrides. For these molecules potential curves and various properties were computed. The characteristic of the chemical binding and the electronic charge distribution has been analyzed extensively. Electron affinities for CH, NH, OH and SiH, PH and SH have been computed in the Hartree-Fock approximation, and corrected empirically for the correlation error inherent in the Hartree-Fock approximation. In the case of polyatomic systems, wavefunctions for

CH_3 and OH_3^+ were obtained using the one center expansion method and the Hartree-Fock approximation.

A careful study of the 2 and 4 electron atoms and ions has been undertaken, in order to assess the value of the MC-SCF model and its efficiency in accounting for electron-electron correlation. Preliminary calculations, using the MC-SCF model, have been performed for several low lying states of LiH and BeO. These calculations are still preliminary. However, indications are that in the case of LiH potential curves for several low lying states can be obtained with an accuracy of a few 100 cm^{-1} without excessive computational effort.

3. Calculation of Transition Moments

Computer programs for the calculation of absolute line strength of electronic and vibration-rotational spectra of diatomic molecules have been developed. These programs require as input information the molecular electronic energy and wave function at various internuclear distances. With this the rotation-vibration wave functions and line intensities, f-numbers, are calculated.

To date the vibrational transition probabilities of the $X^1\Sigma^+$ electronic ground states of BeO, MgO, CaO and SrO have been calculated using HF electronic wave functions and potential curves as well as experimental RKR potential curves. The detailed results of these calculations have been written up for publication.

In addition, the calculation of transition moments, in dipole length and momentum representation of

$$BeH \qquad (A^2\Pi \quad — \quad X^2\Sigma^+)$$

$$MgH \qquad (A^2\Pi \quad — \quad X^2\Sigma^+)$$

$$OH \qquad (A^2\Sigma^+ \quad — \quad X^2\Pi)$$

$$N_2^+ \qquad (A^2\Pi_u \quad — \quad X^2\Sigma_g^+)$$

$$(B^2\Sigma_u^+ \quad — \quad X^2\Sigma_g^+)$$

$$N_2 \qquad (B^3\Pi_g \quad — \quad A^3\Sigma_u^+)$$

is in progress. A report of the results obtained, together with a critical review of the reliability of measured and computed transition probabilities, has been completed.

4.   Numerical SCF for Atoms

An extensive and thorough study was carried out re-examining the classical approach of Hartree and Fock to calculate atomic wave functions. In the course of this work, many refinements to the theory were discovered which influence numerical computations considerably, especially for heavier atoms.

The generally accepted formulas for the orbitals in the regions $r \to o$ and $r \to \infty$ were found to be in error; the correct formulas were derived, and they

yielded some surprising results. For example, it was found that for $r \to \infty$ all orbitals ultimately decay with a decay constant appropriate to the weakest bound electron.

New formulas and techniques were derived which facilitated the adjustment of orbital energies, and also for matching the inner and outer portions of the wave functions.

Additional work is necessary before a computer program can be completed based on this analysis. This is expected to be accomplished in the near future. Calculations of much greater accuracy and reliability than carried out to date will then be possible.

5.   Variational Treatment of Electron-atom Scattering and
      Atomic Resonance States

Two complimentary efforts were undertaken in this area. One involved the numerical determination of orbital and scattering wave functions, the other an expansion technique similar to the LCAO-SCF procedure. Both efforts are based on a wave function of great flexibility, in order to overcome the inherent limitations in close coupling and related methods commonly used. Much attention was paid to avoid the numerical difficulties encountered by singular behavior of the mathematical formalism, which have so often been encountered in calculations of this type. Papers describing these efforts will be forthcoming in the near future.

6.   Relativistic Calculation on Atoms

The commonly used approaches to calculate relativistic wave functions
for atoms were carefully examined. It was found that up to order $(v/c)^2$ the
relativistic corrections are best calculated by the straightforward generalization of
the Pauli approximation to the many-electron case. Hence all relativistic corrections--
to this order of accuracy--can be determined as expectation values using non-relativistic
Schrödinger wave functions and appropriate operators. It is also shown that this formalism
can be applied to wave functions of great generality; in particular, MC-SCF wave
function can be used with ease in order to calculate relativistic corrections with great
accuracy.

Calculations of level splittings for several atoms with low Z have been
carried out, and are continuing. A paper describing the theory and the corresponding
calculations is nearing completion.

7.   Atomic and Molecular Polarizabilities

Polarizabilities of atoms had been calculated successfully in this
laboratory using the coupled Hartree-Fock formalism. Present investigations concen-
trate on using wave functions of much greater generality. Very accurate polarizabilities
have been calculated for a few light atoms, and work on other atoms and the N_2
molecule is in progress.

In connection with this work, several interesting theoretical results have been derived, using Hellman-Feynman—, hypervirial —, and other well-known theorems.

8.   Accurate Wave Functions for the H_2 Molecule

Further work on the H_2 molecule, in particular for excited states of interest, was carried out by Drs. Kolos and Wolniewicz. All this work has now been published, and need not be summarized separately.

PERSONNEL ASSOCIATED WITH CONTRACT

STAFF

Professor Clemens C. J. Roothaan, Principal Investigator, June 12, 1966 to June 11, 1970.

Professor Ugo Fano, Principal Investigator, June 12, 1967 to June 11, 1969.

Professor Juergen Hinze, Research Associate, June 12, 1966 to June 11, 1967; Principal Investigator, June 11, 1967 to June 11, 1970.

Professor Robert S. Mulliken, Consultant, from June 12, 1966 to June 11, 1968.

Professor Wlodzimierz Kolos, Visiting Associate Professor of Physics, Summer 1966 and from June 1, 1967 to January 31, 1968.

Dr. Paul Cade, Physicist, from June, 1966 to August 25, 1969.

Dr. Nora Sabelli, Chemist, from January 15, 1967 to June 11, 1969.

RESEARCH ASSOCIATE

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Paul E. Bagus, from 9/27/67 to 6/30/68.

William H. Henneker, from 1/15/68 to 12/31/69.

Herbert E. Popkie, from 11/1/67 to 6/11/70.

Roy Wessel, from 6/66 to 9/1/66.

Lutoslaw Wolniewicz, from 7/17/67 to 2/29/68.

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Edward Weiss, from 6/67 to 6/11/70. Physics Ph.D. Candidate.

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TECHNICIANS

Tracey Kinyon, Mathematics Assistant, from June, 1966 to June 30, 1967.

Thomas Sherrard, Programmer, from June, 1966 to December 31, 1966.

PUBLICATIONS

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2. Y.-K. Kim. "A Relativistic Self-Consistent-Field Theory for Closed Shell Atoms", Phys. Rev. 154, 17 (1967).

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LMSS JOINT TECHNICAL REPORTS

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